

Conference Paper

Sorption Properties of the Filter Material MS in Relation to Copper(II) Ions

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Abstract

The sorption of copper(II) ions by the mineral filter material MS was studied. The study was carried out on a model solution of copper(II) sulfate containing an additional 400 mg/dm³ of sodium sulfate. It demonstrates that the sorption properties of MS are due to the simultaneous action of two factors. The first is associated with an increase in the pH of the solution being purified when the MS material is introduced into it, which leads to the precipitation of copper(II) ions from the solution in the form of the corresponding hydroxide. The second is the ability of the MS to remove copper(II) ions from the solution by the mechanism of adsorption described by the Langmuir equation. It was found that with an increase in the pH of the solution from 4 to 6.7, the adsorption of copper(II) ions on the surface of the MS increases (ranges of pH<4 and pH>6.7 have not been studied). The found values of the MS monolayer capacity with respect to copper(II) ions turned out to be comparable in magnitude with similar values for some other mineral sorbents.

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1. Introduction

The problem of wastewater and polluted natural waters purification from heavy metal ions is very important for the Ural region. The problem is especially acute of purification of waste water from copper ions before dumping them into natural reservoirs with fishery purposes, for which extremely low MPC values (Russia) of 0.001 mg/dm³ are established [1]. For comparison, the MAC of hexavalent chromium for the same reservoirs is already 0.02 mg/dm³. For zinc, nickel and iron ions, the MAC value is also about an order of magnitude higher than for copper ions.

Meanwhile, for the treatment of wastewater from heavy metals in most industrial enterprises, the traditional method is used, which consists in the treatment of wastewater with lime milk, which leads to an increase in the pH of the solution to 8-10 values and the subsequent precipitation of the corresponding metal hydroxides. However, this method cannot ensure the treatment of wastewater from copper(II) ions to the MPC level for fishery reservoirs. Practice shows that the residual concentration of copper in

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contaminated solutions after their treatment with milk of lime is about 0.1-0.2 mg/dm³ [1], which is in good agreement with the corresponding theoretical calculations [2].

The most promising method of solving the problem is, in our opinion, a sorption method of purification of contaminated water. One of the advantages of this method is that it practically does not change the salt content of the solution being purified, since it does not introduce new ions into it. This makes it possible to use this method for cleaning not only sewage, but also polluted natural waters for their subsequent use in municipal services.

The aim of this work is to study the sorption properties of industrial mineral filter material (sorbent) MS produced by *ALSIS JSC* (Ekaterinburg), in relation to copper(II) ions. This material is recommended by the manufacturer to clarify water and purify it of iron, manganese, hydrogen sulfide and petroleum products. Its sorption properties with respect to copper(II) ions and other heavy metal cations are not well understood.

2. Experimental

The filtering mineral material (sorbent) MS is a brown powder. A fraction with a size of 0.315-0.7 mm was taken for the study. The experiments were carried out on a model aqueous solution simulating natural and waste waters, which was prepared by dissolving sodium and copper sulfates (Na₂SO₄ and CuSO₄) in distilled water. The concentration of sodium sulfate in the model solution was 400 mg/dm³, and copper(II) ions varied in different experiments, but did not exceed 15 mg/dm³. All experiments were carried out at room temperature (25±2 °C) and continuous stirring with a magnetic stirrer of the model solution into which the sorbent was added. Then, after 30 minutes of exposure of the sorbent in the stirred solution, a sample was taken from it for analysis. The concentration of copper(II) ions in the solution was determined by a photocolorimetric method with sodium diethyldithiocarbamate on a photocolorimeter KFK-2 (Russia) [3].

The main experiments were performed at different pH values of the solution. At the same time, the pH of the solution was adjusted to the required value only after the sorbent was introduced into the model solution, and the pH of the solution was then maintained at a given level using an ANION 4100 pH instrument (Russia) and 0.1 N solutions of sulfuric acid and NaOH. It should be noted that in these and other similar experiments, the electrodes of the pH instrument were constantly immersed in the model solution with the sorbent throughout the entire experiment. X-ray phase analysis of the obtained powders was performed on a Dron-6 diffractometer (Russia) in Ka-Cu radiation. The specific surface of the powder of MS (of 13.05 m²/g) and pore volume (3,73·10⁻⁴ cm³/g) was determined by the BET method by nitrogen adsorption

on a Gemini VII 2390 V1.03 (USA) installation. Chemical analysis of the filter material MS was performed according to standard methods with the transfer of the solid phase into solution and its subsequent analysis by the atomic adsorption method.

3. Results and Discussion

The results of chemical and x-ray analysis of the sorbent MS are given below in Tables 1 and 2, from which it follows that the sorbent MS consists mainly of magnesium silicates (forsterite and lizardite) and a small impurity of magnetite. In addition, the MS contains a small amount of some calcium- and aluminum-containing minerals that could not be determined by X-ray phase analysis (Table 2).

TABLE 1: Results of X-ray phase analysis of the sorbent MS.

Detected phase	Quantity, mass. %
Mg_2SiO_4 (forsterite)	98.31
$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ (lizardite)	0.51
Fe_3O_4	1.19

TABLE 2: Results of chemical analysis of the sorbent MS.

Component	Al	Ca	Fe	Mg	Si
Content, mass. %	0.8	0.4	6.4	22.8	15.9

When the sorbent was aged in distilled water, an increase in pH to values of 9-10 depending on the concentration of MS in the solution was found, apparently due to the partial dissolution of magnesium silicates and calcium compounds in it. A chemical analysis of distilled water after holding MS in it showed the presence of calcium ions (3 mg/dm^3), magnesium (10.9 mg/dm^3) and silicon (9.05 mg/dm^3) in the solution.

It is obvious that the increase in the pH of the solution caused by the introduction of the MS sorbent into it will lead to the fact that unwanted impurities, in the form of heavy metal cations contained in the contaminated solution, will precipitate in the form of corresponding hydroxides. Thus, it can be assumed that the effect of cleaning contaminated solutions from this type of impurities when using MS material can be caused not only by their adsorption on the surface of the sorbent, but also by an increase in the pH of the solution. This effect is well demonstrated in Figure 1, which shows the residual concentration of copper(II) ions in the model solution during its alkalization (without the introduction of the filter material MS) and when the sorbent MS is introduced into the solution. In the first case, a NaOH solution was slowly added to the model solution to increase the pH, and after 30 minutes of exposure, a sample was taken for analysis. In the second case, the sorbent MS was added to the model

solution and after 30 minutes of exposure of the sorbent in the stirred solution, the pH of the latter was measured and the sample was also taken for analysis. For experiments with the addition of MS, Figure 1 shows the concentration of the sorbent in the solution at each test point.

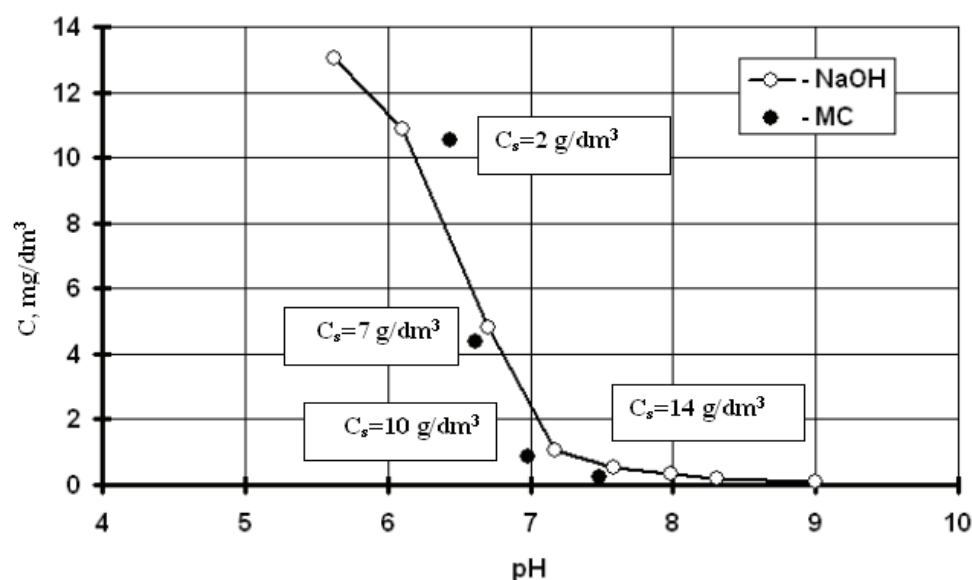


Figure 1: Influence of pH and concentration (C_s) of the sorbent MS in the model solution on the residual content (C) of copper(II) ions in it (initial concentration of copper(II) ions in solution was 12.72 mg/dm^3).

The experimental points for both series of experiments, regardless of how the given pH of the solution was achieved (introducing alkali into the model solution or adding the MS sorbent to it), fell almost on the same curve (the discrepancies are within the experimental error). This confirms that the removal of copper(II) ions from the solution being purified when MS material is added to it occurs mainly due to an increase in pH (which leads to the precipitation of copper hydroxide). The effect of adsorption on the process of cleaning the solution of copper(II) ions is apparently insignificant. Recalculation of the obtained experimental data was carried out according to the classical Langmuir equation for monomolecular adsorption:

$$A = A_{\infty} \frac{K \cdot C}{1 + K \cdot C}, \quad (1)$$

where A is the adsorption value, mg/g or mg/m^2 ; A_{∞} is the capacity of adsorption monolayer of the sorbent, mg/g or mg/m^2 ; K is the adsorption equilibrium constant, dm^3/mg).

On the graph in coordinates of $1/A - 1/C$ (Figure 2), the calculated points are well approximated by a straight line (correlation coefficient 0.90), confirming the validity of Eq.(1). Hence, if we do not take into account the results presented in Figure 1, we can

make an erroneous conclusion about the removal of copper(II) ions from the solution being purified due to their adsorption on the surface of the sorbent MS.

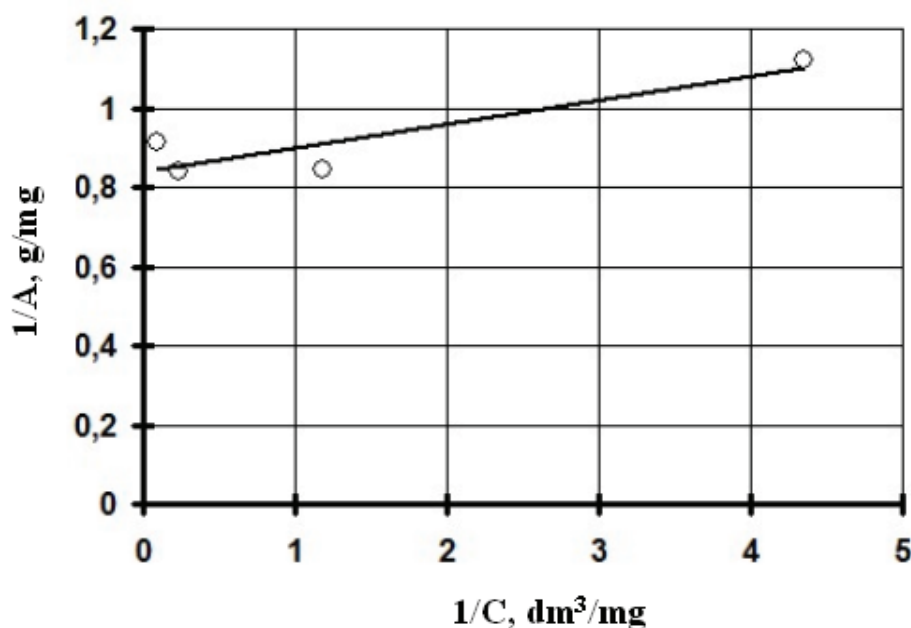


Figure 2: Experimental data on the deposition of copper(II) ions from the model solution at the introduction of the sorbent MS in it in the coordinates of the transformed Eq. (1).

In order to determine the contribution of adsorption to the removal of copper(II) ions from the solution using MS filter material, experiments were conducted in which the pH was maintained on a constant level by adjusting by solutions of sulfuric acid and caustic soda. In addition, the concentration of copper(II) ions was reduced so as to eliminate its deposition from the solution in the form of hydroxide. Such setting of experiments allowed to exclude the influence of the factor of increase in pH of solution (at introduction MS in it) on removal of copper from solution.

Some results of these experiments are shown in Figure 3 in the coordinates of the linear form of Eq. (1). As you can see, the experimental points fit well on a straight line. This indicates that the MS filter material is able to remove copper(II) ions from the contaminated solution not only by increasing its pH, but also by adsorption on its surface.

The obtained data allowed to calculate the parameters of the Langmuir equation (Table 3). Note that at $\text{pH} < 4$ the adsorption of copper(II) ions by the MS filter material was not studied in the present work.

It can be seen from the above data that the capacity of the adsorption monolayer of the material MS increases sharply with increasing pH of the solution. At the same time, an increase in the adsorption equilibrium constant is observed. At $\text{pH} > 6.7$, reliable results

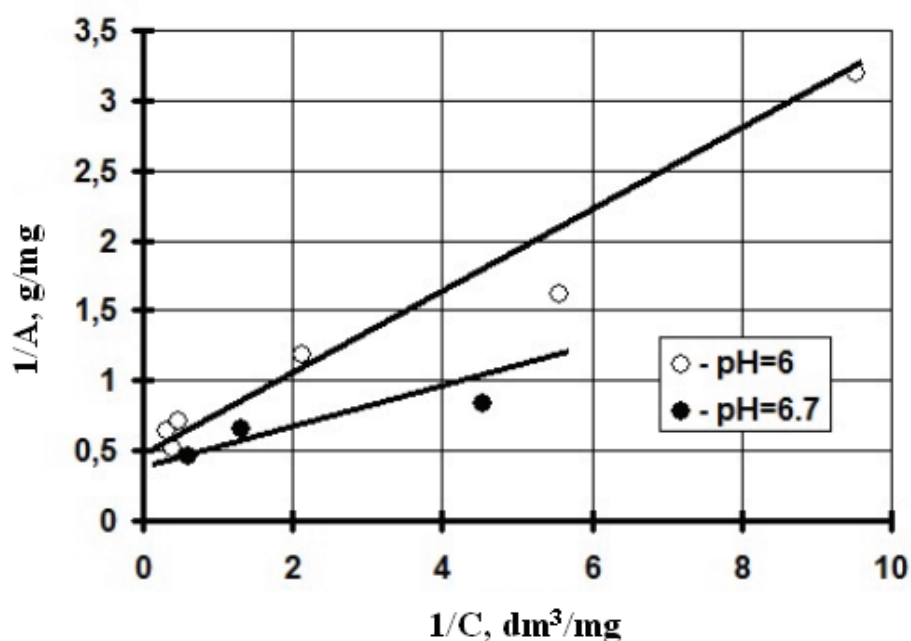


Figure 3: Experimental data on the sorption of copper(II) ions from the model solution at pH 6 and 6.7 by the sorbent MS in the coordinates of the linear form of Eq. (1).

TABLE 3: Dependence of the parameters of Eq. (1) on the pH of the solution in which the sorption of copper(II) ions occurs (R_c is the correlation coefficient).

pH	$A_{\infty}, \text{mg/g}$	$A_{\infty}, \text{mg/m}^2$	$K, \text{dm}^3/\text{mg}$	R_c
4	0.7945	0.0609	0.1175	0.966
5	0.7696	0.0509	0.6695	0.904
6	2.0036	0.1535	1.8841	0.981
6.7	2.5400	0.1946	2.8919	0.982

were not obtained due to a large experimental error in determining the concentration of copper(II) ions in solution.

According to the data given in [4, 5], the capacity of the monolayer of various mineral sorbents with respect to copper(II) ions lies in the range from 1.01 to 55.56 mg/g. Thus, the filter material MS in its sorption properties is comparable with other mineral sorbents.

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